PCT/GB 00/ 03184

10/049604

GB00/03184

INVESTOR IN PEOPLE

The Patent Office
Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

PRIORITY DOCUMENT

SUBMITTED OR TRANSMITTED IN COMPLIANCE WITH RULE 17.1(a) OR (b)

REC'D 12 SEP 2000

WIPO PCT

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

I also certify that by virtue of an assignment registered under the Patents Act 1977, the application is now proceeding in the name as substituted.

I also certify that the attached copy of the request for grant of a Patent (Form 1/77) bears an amendment, effected by this office, following a request by the applicant and agreed to by the Comptroller-General.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

[redacted]egistration under the Companies Act does not constitute a new legal entity but merely [redacted]ects the company to certain additional company law rules.

Signed

Dated 29 AUG 2000

GB9919304.7

By virtue of a direction given under Section of the Patents Act 1977, the application is proceeding in the name of

INEOS ACRYLICS UK LIMITED
P O Box 90
Wilton Centre
Middlesbrough
CLEVELAND
TS90 8JE
United Kingdom
[ADP No. 07841661001]

Patents Form 1/77

Patents Act 19..
(Rule 16)

The Patent Office

THE PATENT OFFICE
K
17 AUG 1999
RECEIVED BY POST

1/77

UG99 E469859-1 D02877
01/7700 0.00 9919304.7

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

The Patent Office
Cardiff Road
Newport
Gwent NP9 1RH

1. Your reference — MTW50830

2. Patent application number *(The Patent Office will fill in this part)* — **9919304.7** — 17 AUG 1999

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

IMPERIAL CHEMICAL INDUSTRIES PLC
IMPERIAL CHEMICAL HOUSE
MILLBANK, LONDON SW1P 3JF
UNITED KINGDOM

4/2/00

SECTION 30 (1) (a) APPLICATION FILED

Patents ADP number *(if you know it)* 935003

If the applicant is a corporate body, give the country/state of its incorporation — UNITED KINGDOM

4. Title of the invention — ACRYLIC COMPOSITION

5. Name of your agent *(if you have one)* — Sara Hillary Margaret GIBSON

Form 5/77

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

ICI Group Intellectual Property
PO Box 90
Wilton, Middlesbrough
Cleveland, TS90 8JE
United Kingdom

Applegard Lees
15 Clare Road
HALIFAX
HX1 2HY

190001

Patents ADP number *(if you know it)*

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*

a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
c) any named applicant is a corporate body.
See note (d))

YES

Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form	
Description	7
Claim(s)	1
Abstract	1
Drawing(s)	

10. If you are also filing any of the following, state how many against each item.

Priority documents	
Translations of priority documents	
Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	
Request for preliminary examination and search *(Patents Form 9/77)*	
Request for substantive examination *(Patents Form 10/77)*	
Any other documents *(please specify)*	

11. I/We request the grant of a patent on the basis of this application.
IMPERIAL CHEMICAL INDUSTRIES PLC
Signature S H M Gibson Date 16 August 1999

12. Name and daytime telephone number of person to contact in the United Kingdom
S H M GIBSON
(01642) 436282

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

a) If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.

b) Write your answers in capital letters using black ink or you may type them.

c) If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.

d) If you have answered 'Yes' Patents Form 7/77 will need to be filed.

e) Once you have filled in the form you must remember to sign and date it.

f) For details of the fee and ways to pay please contact the Patent Office.

Acrylic composition

The present invention relates to acrylic compositions and in particular to acrylic compositions for making articles having surfaces exhibiting relatively low gloss compared to articles made from conventional acrylic compositions.

Acrylic compositions are used in a variety of applications, some of which may demand a particular surface appearance, such as low gloss. Acrylic compositions containing gloss modifiers, usually to reduce the surface gloss of the composition, are already known and used in the industry. A common example of a gloss modifying compound is talc. When a very low gloss or matte surface finish is required, e.g. for use as building components, conventional gloss reducing compounds may be ineffective or may be required to be present at such high levels that the other properties of the composition are compromised. There is therefore a need for an acrylic composition which is suitable for producing articles which have a relatively low gloss surface but which are comparable in physical properties to higher gloss acrylic compositions.

WO-A-97/14749 describes acrylic compositions having the appearance of a natural granite comprising a polymethyl methacrylate matrix having dispersed within it particles comprising 75 - 90 wt % of PMMA and at least 10 % of an ethylenically unsaturated comonomer and at least 0.4 wt % of a cross-linker. The granite articles are prepared by casting a syrup of polymer in monomer containing the particles and curing to produce a glossy article.

US-A-5242968 describes a cast acrylic article having a textured but glossy surface formed by casting a polymer in monomer syrup containing ground PMMA particles in a cell and curing the mixture so that it polymerises.

US-A-5304592 describes acrylic articles which contain particles of a thermoplastic and/or thermoset plastic which are visually different from the acrylic matrix in which they are suspended and which have different viscosities or melting points from the plastic of the matrix yet which have a similar density to the matrix so that the particles do not settle during processing.

According to the present invention we provide a melt-processable thermoplastic composition comprising

a) 50 - 99.5 wt % of a melt-processable thermoplastic polymer and

b) 0.5 - 50 % wt of a particulate polymer comprising the residues of a monomer mixture comprising 50 - 100 wt % of PMMA, at least 0 - 50 % of an ethylenically unsaturated comonomer comprising at least one alkyl acrylate or methacrylate and 0 - 10 wt % of a copolymerisable cross-linking monomer said particles having a maximum dimension of 5 mm.

We have found that the incorporation of the particulate polymer into the PMMA polymer matrix enables articles to be produced by melt-processing techniques such as injection moulding or extrusion, which have an excellent low-gloss surface finish.

Accordingly we also provide an article formed by shaping a molten thermoplastic composition formed by melting an acrylic composition comprising

a) 50 - 99.5 wt % of a melt-processable thermoplastic polymer and

b) 0.5 - 50 % wt of a particulate polymer comprising the residues of a monomer mixture comprising 50 - 100 wt % of PMMA, at least 0 - 50 % of an ethylenically unsaturated comonomer comprising at least one alkyl acrylate or methacrylate and 0 - 10 wt % of a copolymerisable cross-linking monomer said particles having a maximum dimension of 5 mm.

The article need not be entirely formed from the molten thermoplastic composition. There are many applications in which an article may comprise other materials, e.g. it may be a laminate of the thermoplastic composition and another material or the thermoplastic composition of the invention may form only a surface coating on an article. Such composite articles may be formed by forming a separate thermoplastic layer and bonding it to the finished article or the thermoplastic layer may be applied by techniques such as coextrusion with another thermoplastic or by extrusion coating.

The thermoplastic polymer forms a matrix throughout which the particulate polymer is dispersed. The particulate polymer may, however be more or less concentrated in some parts of the matrix than others as a result of the melt-processing method used to form the article.

The melt-processable polymer may be selected from a range of materials, e.g. PVC, polystyrene, polyesters, styrene - acrylonitrile copolymers and terpolymers, e.g. ABS,

styrene - acrylonitrile (SAN), acrylonitrile - styrene - acrylic (SAN), polycarbonate, nylon, acrylic polymers such as polymethylmethacrylate and its copolymers with other (meth)acrylates, provided that the polymer(s) selected may be melt processed at a temperature which is below the temperature at which the particulate acrylic polymer thermally degrades, e.g. below about 300 °C. The melt-processable polymer may also comprise a blend of thermoplastic polymers. In one preferred form of the invention the thermoplastic matrix polymer is a polymethylmethacrylate (PMMA) homopolymer or copolymer derived from a monomer mixture comprising 60 - 100 wt% methyl methacrylate and 0 - 40 wt % of at least one other copolymerisable alkyl acrylate or methacrylate. A preferred PMMA matrix is a copolymer of 60 - 98 wt% methyl methacrylate and 2 - 40 wt % of at least one other copolymerisable alkyl acrylate selected from methyl, ethyl, butyl, hydroxyethyl, 2-ethylhexyl, cyclohexyl or phenyl acrylates. A preferred copolymer comprises 80 - 98% methyl methacrylate residues and 2 - 20 % of the residues of at least one alkyl acrylate. The matrix polymer may additionally contain residues of other materials, e.g. thermal stabilisers (e.g. alkyl mercaptans as are commonly used in moulding polymer formulations), polymerisation initiators, lubricants, mould release agents, UV and light stabilisers, pigments, dyes, opacifiers, impact modifying compounds (including rubbery materials and core-shell type impact modifying particles) and flame retardents.

The particulate polymer is a homopolymer or copolymer of comprises 50 - 100 wt % of MMA, at least 0 - 50 % of an ethylenically unsaturated comonomer comprising at least one alkyl acrylate or methacrylate and 0 - 10 wt % of a copolymerisable cross-linking monomer . Suitable particles are described in WO-A-97/14749 for incorporation into cast acrylic products to impart the appearance of granite. Preferred particles are formed from the residues of a monomer mixture comprising 70 - 95 % wt methyl methacrylate (MMA), 5 - 30 % of a copolymerisable acrylic comonomer (preferably an alkyl acrylate) and 0.1 - 5 % of a comonomer which is capable of forming cross-linking within the polymer. Particularly suitable cross-linking comonomers are multifunctional acrylate monomers, e.g. dimethacrylate compounds.

Preferably the particulate material is present at a concentration of 5 - 40 e.g. 10 - 30 wt % of the acrylic composition. The polymer particles may have a wide size distribution and have a maximum size of about 5 mm. Preferably the particles have a maximum dimension which is less that 1 mm, for example particles which pass though a 500 μm

sieve may be from used. In one preferred form particles having a size distribution from <10 to about 600 μm are used. We have found that in high shear processes such as extrusion, the particles are broken up into smaller particles so that surprisingly, the particles do not produce an unduly rough or lumpy surface, even when particles as large as 250 μm are incorporated into an extruded layer of the thermoplastic composition having a thickness below 100 μm. Therefore it is expected that the particle size to be used will depend upon its availability and the constraints of handling and processing such particles.

The polymer particles are preferably made by grinding a larger piece or pieces of polymer of the required composition. We have found that the particles formed in this way are irregular with many corners and sharp edges. The polymer may be made by a variety of polymerisation methods, e.g. suspension, solution, emulsion, or bulk polymerisation methods.

We have found that when a sheet of the thermoplastic polymer composition has been extruded and calendered, there are marked differences between the gloss on the surface of the sheet which has been in contact with the calender rolls and the opposite surface which has been in contact with air. For this reason, when the low-gloss thermoplastic composition of the invention is applied over a layer of a different polymer, e.g. by coextrusion, it is preferred that the surface of the low-gloss composition is processed so that it is run through the calender roll stack on the air side of the sample.

The invention will be further described in the following examples.

Example 1

A mixture containing a 92 % wt commercial acrylic polymer DIAKON™ MG102 (ICI Acrylics) which is a copolymer of methyl methacrylate and ethyl acrylate and has a molecular weight of approximately 90,000 and 8% of a white pigmented masterbatch was compounded together and pelleted using a Werner & Pfleiderer ZSK30 30mm twin screw extruder running at 230 °C and 275 rpm. The resulting pellets were extruded into a 1mm thick x 100 mm wide sheet using a 1.5" (30mm) single screw extruder operating at 230 °C and at a line speed of approximately 1 m/minute. The extruded sheet was run through a 3-roll calendering stage upon exit from the extruder. The rolls were heated to about 80 °C and were 50mm in radius.

The gloss of each surface of the sheet was measured using a Rhopoint Novo-Gloss meter measuring at an angle of 60°. As will be understood by those experienced in the art of extruding thermoplastic sheet, one surface is in contact with the heated calendering rolls for longer than the other surface and so these surfaces were measured separately. the surface in contact with the rolls for the longest time is referred to as "highly calendered (hc)" whilst the other surface is referred to as "less calendered (lc)". The gloss of each surface was measured at 10 positions along the direction of extrusion of the sheet and the average result is shown in the table.

Preparation of cross-linked acrylic particles

A cross-linked acrylic polymer was made by bulk polymerisation in a sealed nylon bag a monomer mixture comprising 83 % MMA, 8 % n-butyl acrylate, 8 % ethyl acrylate and 1 % ethylene glycol dimethacrylate together with initiators and stabilisers. The mixture was subjected to a pre-programmed thermal cycle as conventionally used for bulk polymerisation processes and then cooled. After cooling to ambient temperature, the bag and thermocouple were removed and discarded. The resultant polymer was ground and sieved with a standard wirecloth sieve. The sieve fractions which passed through a standard US 60 mesh sieve (aperture size 250 μm) were used for these Examples. Particle size analysis showed that 82% of the particles were between 60 (250 μm) and 80 (177 μm) mesh. The particles appeared to be of irregular shape approximating to pyramidal.

The particles of cross-linked acrylic polymer were added to the polymer and colour masterbatch mixture. The mixture was compounded and pelletised and then sheet samples were extruded and their gloss measured .

Table 1

particle content (wt %)	surface	Gloss units
0	hc	87
	lc	87
10	hc	65
	lc	46
20	hc	48
	lc	26

The results show that the presence of the cross-linked acrylic particles reduced the gloss of both of the surfaces of the extruded sheet significantly. The difference in gloss between the surfaces of the same sheet was also noticed for those samples which contained the particles but not for the sample containing no particles. Examination of the samples showed that the shape of the particles had not been changed significantly but their size had been reduced to about 50 - 70 μm.

Example 2

PVC pellets (EVC Compounds RG7-760-1476) were tumble blended with cross-linked acrylic particles as described above and extruded into sheet at 180 °C. A sample without particles was made in the same way. The gloss was measured and the results are shown in Table 2.

Table 2

particle content (wt %)	surface	Gloss units
0	hc	80
	lc	37
10	hc	54
	lc	20
20	hc	11
	lc	8.5

Example 3

Particles of a green coloured cross-linked acrylic polymer were made from a monomer mixture comprising 84% MMA, 15.5 % butyl acrylate and 0.5% ethylene glycol dimethacrylate together with stabilisers, initiators and a chain transfer agent as described earlier. The particles were ground and sieved as before. An impact modified grade of acrylic moulding polymer (DIAKON™ ST35G8) was coloured using a green pigmented masterbatch at 8 % wt. The green particles were compounded into the base polymer on the twin screw extruder and the resulting pellets were injection moulded using a Colourstubbe injection moulding apparatus at 230 °C to form a 75 x 50 x 3 mm plaque sample. The gloss was measured as described earlier and the results are shown in Table 3.

Table 3

particle content (wt %)	Gloss units
0	85
5	15
10	8
20	7

Claims

1. A melt-processable thermoplastic composition comprising

a) 50 - 99.5 wt % of a melt-processable thermoplastic polymer and

b) 0.5 - 50 % wt of a particulate polymer comprising the residues of a monomer mixture comprising 50 - 100 wt % of MMA, at least 0 - 50 % of an ethylenically unsaturated comonomer comprising at least one alkyl acrylate or methacrylate and 0 - 10 wt % of a copolymerisable cross-linking monomer said particles having a maximum dimension of 5 mm.

2. A composition as claimed in claim 1, wherein the particulate polymer is a copolymer of 70 - 95 % wt methyl methacrylate (MMA), 5 - 30 % of a copolymerisable acrylic comonomer (preferably an alkyl acrylate) and 0.1 - 5 % of a comonomer which is capable of forming cross-linking within the polymer.

3. An article formed by shaping a molten thermoplastic composition formed by melting an acrylic composition comprising

a) 50 - 99.5 wt % of a melt-processable thermoplastic polymer and

b) 0.5 - 50 % wt of a particulate polymer comprising the residues of a monomer mixture comprising 50 - 100 wt % of PMMA, at least 0 - 50 % of an ethylenically unsaturated comonomer comprising at least one alkyl acrylate or methacrylate and 0 - 10 wt % of a copolymerisable cross-linking monomer said particles having a maximum dimension of 5 mm.

Abstract

A melt-processable thermoplastic composition is described, which comprises

a) 50 - 99.5 wt % of a melt-processable thermoplastic polymer and

b) 0.5 - 50 % wt of a particulate polymer comprising the residues of a monomer mixture comprising 50 - 100 wt % of MMA, at least 0 - 50 % of an ethylenically unsaturated comonomer comprising at least one alkyl acrylate or methacrylate and 0 - 10 wt % of a copolymerisable cross-linking monomer said particles having a maximum dimension of 5 mm. The compositions have reduced surface gloss and may be useful for forming building components or in any other application in which a low gloss surface is required.

PCT NO : GB00 03184

FORM 23/77 : 16.8.00

AGENT : Applegarth Legs